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Long-range Magnetic Interactions (RKKY-type) in the UP-US Solid Solutions*

Abstract: UP, US, and the UP-US solid solutions have the NaCl-type structure and are good conductors of electricity. UP is antiferromagnetic of type I; US is ferromagnetic. Assuming U^{4+} cations, P^{3-} and S^{2-} anions, and RKKY interactions between the uranium localized 5f-electrons via the conduction electrons (≈ 1 in UP and ≈ 2 in US), the observed magnetic structures are accounted for, although these structures are also predicted by molecular field theory. A neutron diffraction study of the UP-US solid solutions has revealed two new magnetic structures, the type IA (2+, 2−) antiferromagnetic structure and the antiphase (5+, 4−) ferrimagnetic structure, which are of long range (several lattice parameters) and are typical of long-range RKKY-type interactions, as assumed in the simple model for these compounds. Further experimental evidence is given for the long-range magnetic interactions in uranium monopnictides and monochalcogenides and their solid solutions. The situation in these uranium compounds is compared with the corresponding lanthanide compounds, and the role of covalency and superexchange in the case of heavier anions is discussed.

Introduction

Studies of the magnetic and electronic properties of lanthanide monopnictides and monochalcogenides (denoted† by Lnv and Lnvi, respectively, and by LnX when referring to both) have been carried out for at least ten years, and lately have become quite intensive and sophisticated. These studies have been reviewed by several authors.[1,2] Investigations of the corresponding actinide compounds are scarce; only for uranium have a relatively large number of studies been made, which are summarized elsewhere.[3,4]

Although uranium metal does not contain localized moments, uranium is the first actinide element that possesses localized 5f-electrons in its compounds, especially in uranium monopnictides and monochalcogenides (denoted by Uv and Uvi, respectively, and by UX when referring to both). All the UX compounds have the NaCl-type structure, like most of the LnX. While all the UX compounds are good conductors of electricity (room-temperature resistivities of 150–300 $\mu\Omega$cm), and their resistivity curves indicate magnetic ordering, some of the LnX are semiconductors. The high ordering temperatures of the UX compounds indicate a strong magnetic coupling in these compounds. Most LnX compounds have lower ordering temperatures, and some (compounds of Pr, Sm, Eu, Tm and Yb) do not even order due to stronger crystal field effects.

In this paper we summarize some of the results, obtained in several studies[5–9] of the UP-US solid solutions, which show that the magnetic interactions in the UX compounds are of long range. We compare these results with the corresponding results in the LnX compounds.

The UP-US solid solutions

A simple model proposed[3] for the UX compounds assumes that these compounds are built of U^{4+} cations ($5f^2$ configuration), v^{3-} and vi^{2-} anions, and Z conduction electrons (≈ 1 in the Uv compounds, ≈ 2 in the Uvi compounds, and 1-2 in the Uv-Uvi solid solutions). The model assumes the applicability of crystal field theory and Ruderman–Kittel–Kasuya–Yosida (RKKY)-type interactions between the uranium 5f-localized electrons (via the conduction electrons). The model accounts for the rather large U-U distances (shortest interuranium distances of 3.5-4.4Å), the good electrical conductivity, the measured values of the ordered and paramagnetic moments, the type I antiferromagnetic ordering[10] of the Uv compounds, and the ferromagnetic ordering of the Uvi compounds. However, the type I antiferromagnetic structure and the ferromagnetic structure are predicted for fcc materials by the molecular field theory that involves up to fourth-nearest neighbors,[11] and these structures could therefore

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* Based on work performed under the auspices of the U. S. Atomic Energy Commission.

† The notation v, vi, etc. represents unspecified elements occupying positions in the fifth, sixth, etc. column of the periodic table.

indicate short-range superexchange interactions in the UX compounds, such as the popular treatment of some LnX compounds.[1]

Clear evidence for the type of magnetic interactions in the UX compounds is provided by the study of the UP-US solid solutions (the $UP_{1-x}S_x$ system). The compounds UP (U^{4+}, P^{3-}, and $Z \approx 1$) and US (U^{4+}, S^{2-}, and $Z \approx 2$) are completely miscible and the lattice parameter of the solid solutions decreases by less than 2% throughout the system (from 5.589Å in UP to 5.489Å in US) with a slight positive deviation from linear variation.[5] A neutron diffraction study of the $UP_{1-x}S_x$ system[6] has shown that the (P, S) site at all compositions studied is randomly occupied. The UP-US solids solutions (with Z = 1-2) are predicted by the simple model[3] to have more complicated structures than UP (type I antiferromagnetic[10]) and US (ferromagnetic[12]).

The neutron diffraction study[6] has established the magnetic phase diagram of the $UP_{1-x}S_x$ system at zero external magnetic field. The magnetic structures involved are the following:

- $0 \leq x \lesssim 0.05$: Type I antiferromagnetic structure, first observed in UP.[10]
- $0.05 \lesssim x \lesssim 0.10$: Type I antiferromagnetic structure at the temperature range just below the Néel temperature T_N; type IA antiferromagnetic structure[7] at lower temperatures.
- $0.10 \lesssim x \lesssim 0.20$: Type IA antiferromagnetic structure.
- $x \approx 0.25$: Type IA antiferromagnetic structure at temperatures below ≈20°K; ferromagnetic structure at temperature between ≈70°K and T_N(≈100°K); the antiphase (5+, 4−) ferrimagnetic structure[8] at about 20-70°K, found to be metamagnetic.[9]
- $0.28 \lesssim x \leq 1$: Ferromagnetic structure.

The antiferromagnetic structures are built by stacking ferromagnetic sheets of uranium moments, with the moments directed along the cubic [001] axis, perpendicular to the sheets. The ferromagnetic sheets are stacked antiferromagnetically (+−+−) in type I, antiferromagnetically in pairs (++−−) in type IA, and in an antiphase (5+, 4−) arrangement in the ferrimagnetic structure. This ferrimagnetic structure resembles the low-temperature antiphase (4+, 3−) ferrimagnetic structure of thulium.[13]

The two *new* magnetic structures observed in the $UP_{1-x}S_x$ system, the type IA (2+, 2−) antiferromagnetic structure and the antiphase (5+, 4−) ferrimagnetic structure, are indeed more complicated than those of UP and US. The important feature of the new structures is their long range, over several lattice parameters. Such long-range magnetic structures cannot be accounted for by molecular field theory[11] or by superexchange interactions, and are accounted for only by long-range (RKKY-type) magnetic interactions, as postulated in the simple model.[3] Since the variation in lattice parameter in the $UP_{1-x}S_x$ system is negligible, the changes in magnetic structures are a result of varying Z, the concentration of conduction electrons. It is concluded that the dominant magnetic interactions in the UP-US solid solutions, and presumably also in the other UX compounds and their solid solutions, are the long-range RKKY-type interactions. Such interactions determine the ordering in the lanthanides and their metallic compounds.

Further evidence for long-range interactions

The magnetic behavior of UAs[14] is similar to the behavior of the $UP_{1-x}S_x$ system in the compositional range $0.05 \lesssim x \lesssim 0.10$. UAs is type I antiferromagnetic at the temperature range just below T_N; at lower temperatures it has the long-range type IA antiferromagnetic structure. The similarity between UAs and $UP_{0.92}S_{0.08}$ indicates, according to the simple model,[3] a slightly higher value of Z in UAs than in UP. Magnetic measurements[15] on the UAs-USe solid solutions show some metamagnetic behavior at intermediate compositions, which is analogous to the metamagnetism[9] of the ferrimagnetic structure in the UP-US solid solutions. The metamagnetic behavior indicates that besides the type IA, found already in UAs at lower temperatures, the $UAs_{1-x}Se_x$ system has another long-range magnetic structure. The behavior of the $UAs_{1-x}Se_x$ system is further evidence for the dominant role of long-range magnetic interactions in the UX compound and their solid solutions.

Covalency effects; the LnX compounds

In the case of UX compounds with heavier anions, the decrease in electronegativity difference results in some covalency effects. Besides the predominant long-range (RKKY-type) magnetic interactions, the covalency causes short-range magnetic interactions such as superexchange. The effect of the latter is negligible in the Uvi compounds, and among the Uv compounds it is noticed only for USb and UBi,[4] where the ordering (type I) is similar to that of UN rather than UAs. The type I antiferromagnetic structure of USb and UBi is a result of a combined effect of RKKY-type interactions and of superexchange.

The covalency effects are much more pronounced in the LnX compounds,[1] where smaller s-f coupling constants relative to the UX compounds,[3] make the strength of RKKY-type interactions comparable to the strength of the superexchange. We assume that the LnX compounds contain Ln^{3+} cations (Eu^{2+} and Ce^{4+} excepted), v^{3-} and vi^{2-} anions, and a balance of Z conduction electrons. In the Lnvi compounds, which are good conductors of electricity (Euvi excepted), $Z \approx 1$, and the antiferromagnetic ordering predicted by RKKY interactions becomes type II (MnO-type) due to some covalency (e.g. Gdvi compounds[2]). In the Lnv compounds (Cev excepted), which are also good conductors of electricity, $Z \approx 0$, where according to RKKY interactions the ordering should be ferromagnetic, as observed in LnN compounds.[1] The covalency effects turn the ordering of the LnSb and LnBi compounds to type II antiferromagnetic, while LnP and LnAs compounds have intermediate behavior. Among the europium chalcogenides EuO and EuS are ferromagnetic as expected for these semiconductors with $Z \approx 0$ on the basis of long-range RKKY interactions. Such interactions determine the *new*[16] long-range antiferromagnetic structure of type IIA [++−− stacking of ferromagnetic (111) sheets] in EuSe at 2.8-4.6°K. Stronger covalency effects cause the type II antiferromagnetic structure of EuTe. In cerium monopnictides Z is between 0 and 1 (due to existence of Ce^{4+} cations) and the ordering is antiferromagnetic (type I in CeP and CeAs; probably type IA in CeSb[17]).

Summary

Long-range (RKKY-type) magnetic interactions have a dominant role in the UX compounds. This feature is demonstrated by the long-range magnetic structures in the UP-US solid solutions. Covalency effects on the magnetic ordering in the case of heavier anions are minor in the UX compounds and are more pronounced in the LnX compounds.

References

1. G. Busch, *J. Appl. Phys.* **38,** 1386 (1967); S. Methfessel and D. C. Mattis, "Magnetic Semiconductors," in *Encyclopedia of Physics,* S. Flügge, Chief Editor, Vol. XVIII/1 (Magnetism), H. P. J. Wijn, Editor, Springer-Verlag, Berlin 1968, p. 389; P. Junod, A. Menth, and O. Vogt, *Phys. Kondens. Materie* **8,** 323 (1969).
2. T. R. McGuire, R. J. Gambino, S. J. Pickart and H. A. Alperin, *J. Appl. Phys.* **40,** 1009 (1969).
3. J. Grunzweig and M. Kuznietz, *J. Appl. Phys.* **39,** 905 (1968); J. Grunzweig-Genossar, M. Kuznietz and F. Friedman, *Phys. Rev.* **173,** 562 (1968).
4. M. Kuznietz, G. H. Lander and F. P. Campos, *J. Phys. Chem. Solids* **30,** 1642 (1969).
5. Y. Baskin and P. D. Shalek, *J. Am. Ceram. Soc.* **52,** 341 (1969).
6. M. Kuznietz, G. H. Lander and Y. Baskin, *J. Appl. Phys.* **40,** 1130 (1969).
7. G. H. Lander, M. Kuznietz and Y. Baskin, *Solid State Commun.* **6,** 877 (1968).
8. G. H. Lander, M. Kuznietz and D. E. Cox, *Phys. Rev.* **188,** 963 (1969).
9. J. Crangle, M. Kuznietz, G. H. Lander and Y. Baskin, *J. Phys. C. (Solid St. Phys.)* [2] **2,** 925 (1969).
10. S. S. Sidhu, W. Vogelsang and K. D. Anderson, *J. Phys. Chem. Solids* **27,** 1197 (1966); N. A. Curry, *Proc. Phys. Soc. (London)* **89,** 427 (1966).
11. D. ter Haar and M. E. Lines, *Phil. Trans. Roy. Soc. (London)* **A254,** 521 (1962).
12. F. A. Wedgwood (Harwell), "Neutron Diffraction Study of US Single Crystal," (to be published).
13. W. C. Koehler, J. W. Cable, E. O. Wollan and M. K. Wilkinson, *Phys. Rev.* **126,** 1672 (1962).
14. J. Leciejewicz, A. Murasik and R. Troc, *Phys. Stat. Sol.* **30,** 157 (1968).
15. W. Trzebiatowski, A. Misiuk and T. Palewski, *Bull. Acad. Polon. Sci., Ser. Sci. Chim.* **15,** 543 (1967).
16. P. Fischer, W. Hälg, W. von Wartburg, P. Schwob and O. Vogt, *Phys. kondens. Materie* **9,** 249 (1969).
17. B. Rainford, K. C. Turberfield, G. Busch and O. Vogt, *J. Phys. C. (Proc. Phys. Soc.)* [2] **1,** 679 (1968).

Received November 10, 1969